POLYHALOGENATED Ethers

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Field of Classification Search .............. 568/614, 568/615

See application file for complete search history.

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ABSTRACT

(Per)haloethers having formula:

$$X - (R_1)F - O - CF_2 - O - C - X_2 - CF_3 - X_1,$$

process for obtaining them and hypofluorites usable in the synthesis of said (per)haloethers.

20 Claims, No Drawings
OTHER PUBLICATIONS


* cited by examiner
POLYHALOGENATED Ethers

CROSS-REFERENCE TO RELATED APPLICATION

This application is a divisional application which claims the benefit of application Ser. No. 10/357,364, filed Feb. 4, 2003 now U.S. Pat. No. 6,936,722. The disclosure of the prior application is hereby incorporated herein by reference in its entirety.

The present invention relates to (para)haloethers, the process for their preparation and perfluoroalkyl hypofluorites usable in the synthesis of said (para)haloethers.

It is generally stated in the prior art that (para)haloethers, obtained by reacting perfluoroalkyl hypofluorites with (para) halo-olefins, can be used as such or for the preparation of perfluorovinylether monomers. See for example patents U.S. Pat. No. 5,877,357 and EP 683,181. Said monomers are usable in the fluoroclastomer and fluoroplastomer synthesis.

The reaction between the hypofluorite and a (para)haloolefin for the preparation of (para)haloethers is carried out by flowing a gaseous phase, containing the hypofluorite, in the liquid phase containing the (para)halo-olefin at low temperature. See U.S. Pat. No. 5,225,576. To obtain high yields of the sum reaction, it is necessary to work at low temperature. There is however the drawback that an even partial condensation of the hypofluorite can take place before it comes into contact with the olefin. This leads to the hypofluorite decomposition and therefore it can lead to violent explosions. For example, the hypofluorite CF₃CF₂CF₂OF having molecular weight 204 has a boiling point of ~95 0C. (Journal of Fluorine Chemistry, Vol. 95 (1999) 29) and it can easily condensate at the temperatures used in the (para)haloether synthesis. At temperatures lower than ~30 0C the process of the above patent is applicable only to hypofluorites having a low boiling point, i.e., having 1 or 2 carbon atoms in the chain.

Alternatively to the above process, it is known in the prior art that (para)haloethers can be obtained by dissolving the hypofluorite in a suitable halogenated solvent and by adding the solution to the (para)halo-olefin, as for example described in U.S. Pat. No. 4,900,872. From the Examples of said patent the yields are high when perfluoroalkyl hypofluorites having in the chain two carbon atoms are used as hypofluorites. When 1-chloroperfluoroethyl hypofluorite is used, the yields are lower than 30%. Hypofluorites different from (para)fluoroethyl hypofluorites having two carbon atoms are not exemplified. Besides, according to the teaching of said patent, the hypofluorite is synthesized in gaseous phase at low temperature and subsequently is dissolved in an inert solvent up to a concentration of 50% by weight at most.

$\text{CH}_3; -\text{P}(-\text{O})\left(\text{C}_2\text{H}_4\right)_2; -\text{P}(-\text{O})\left(\text{C}_2\text{H}_4\right)_2; -\text{SO}_2\text{F};$ preferably the groups are the following: $-\text{COOR}'_{ib}$ -CN, NCO, NCS, aryl as defined above, $-\text{SO}_2\text{F};$ whereas the remaining substituents of the group of $X_1,$ $X_2,$ $X_3,$ $X_4,$ have the meanings as defined under 1); 3) one of $X_2,$ or $X_4,$ and/or one of $X_1$ or $X_3,$ is chosen from the following groups: 3)a. C$_2$-C$_{20}$ preferably C$_1$-C$_6$, linear or branched per(halo)fluorinated alkyl, preferably (per)fluoroalkyl; 3)b. C$_2$-C$_{20}$ preferably C$_1$-C$_6$, linear or branched per(halo)fluorinated oxyalkyl, preferably (per)fluoroalkyl; 3)c. C$_2$-C$_{10}$ preferably C$_1$-C$_6$, linear or branched alkyl, optionally containing one or more functional groups, chosen between those defined above 3), excluding fluorinated organic anhydrides; wherein the remaining substituents of the group of $X_1,$ $X_2,$ $X_3,$ $X_4,$ have the meanings as defined under 1); 4) one of $X_1,$ or $X_2,$ together with one of $X_3$ or $X_4,$ and the two carbon atoms of the group $-\text{CF}_3, -\text{CF}_3, -\text{CF}_2, -\text{CF}_2, -\text{CF}_2, -\text{CF}_2, -\text{CF}_2, -\text{CF}_2, -\text{CHCl}, -\text{CHFCl},$ wherein the remaining substituents between $X_1,$ or $X_2,$ and between $X_3$ or $X_4,$ have the meanings as defined under 1); 4a) $X_3$ and $X_4,$ together with the relevant carbon atom to which they are attached, form a cyclic anhydride ring having 4 carbon atoms; $X_1,$ and $X_2,$ have the meanings as defined under 1); X has the following meanings: F, linear or branched C$_1$-C$_8$ per(halo)alkyl, preferably (per) fluoroalkyl, wherein optionally one fluorine atom is substituted with one chlorine atom; $-[\text{O}]_{2}\text{CF}_2\text{Cl},$ wherein $T=0$ when $L=1$ and R=R$''$ as defined below; $T=1$ when $L=0,$ when $L=1$ and R=R$''$ as defined below; when $L=1$ and R=R$''$ as defined below, X can also be a C$_2$-C$_{10}$ perfluoroalkyl; L=0, 1, when L=0, from the X meanings the following are excluded: F, $-[\text{O}]_{2}\text{CF}_2\text{OCX},$ $X_1, X_2, X_3, X_4,$ being $T=0,$ $X_1, X_2, X_3, X_4,$ $X_2=$Cl, $X_3, X_4=$F, $X_1, X_2, X_3, X_4, X_2=$Cl, C$_1$-C$_3$ perfluoroalkyl when $X_1, X_2, X_3, X_4, X_2=$Cl; when $L=1$, R=R$''$ for R$''$; being R$''$=C$_2$-C$_{20}$ perfluoroalkylene; R$''$=perfluoroalkylene having formula: $-(\text{OCF}_2\text{CF}_2)_\lambda\text{OCF}_2\text{CF}_2)(\text{OCF}_2\text{CF}_2)_\mu\text{OCF}_2\text{CF}_2)_\nu,$ wherein m, n, p, q, r are integers such that: m is comprised between 0 and 100, extremes included; n is comprised between 0 and 100, extremes included; p is comprised between 0 and 60, extremes included; r is comprised between 0 and 60, extremes included; q is comprised between 0 and 60, extremes included; preferably when R=R$''$, the perfluoroalkylene has the following formula: $-(\text{OCF}_2\text{CF}_2)_\lambda\text{OCF}_2\text{CF}_2)(\text{OCF}_2\text{CF}_2)_\mu\text{OCF}_2\text{CF}_2)_\nu,$ wherein m and n independently from each other have the above values, preferably from 0 to 20; when both m and n are present, m/n ranges from 0.1 to 6. The preferred (per)haloethers of formula (I) are the following:

$$\text{CF}_2\text{CF}_2\text{O}-\text{CF}_2\text{CF}_2\text{O}-\text{CHCl}, -\text{CFCl}, -\text{CFCl};$$
$$\text{CF}_2\text{OCF}_2\text{CF}_2\text{O}-\text{CF}_2\text{CF}_2\text{O}-\text{CFCl}, -\text{CFCl};$$
$$\text{CF}_2\text{OCF}_2\text{CF}_2\text{O}-\text{CF}_2\text{CF}_2\text{O}-\text{CFCl}, -\text{CFCl};$$
$$\text{CF}_2\text{CF}_2\text{O}-\text{CF}_2\text{CF}_2\text{O}-\text{CHCl}, -\text{CHFCl}, -\text{CFCl};$$
$$\text{CF}_2\text{CF}_2\text{O}-\text{CF}_2\text{CF}_2\text{O}-\text{CHCl}, -\text{CHFCl}, -\text{CFCl};$$
$$\text{CF}_2\text{CF}_2\text{O}-\text{CF}_2\text{CF}_2\text{O}-\text{CHCl}, -\text{CHFCl}, -\text{CFCl};$$
$$\text{CF}_2\text{CF}_2\text{O}-\text{CF}_2\text{CF}_2\text{O}-\text{CHCl}, -\text{CHFCl}, -\text{CFCl};$$
$$\text{CF}_2\text{CF}_2\text{O}-\text{CF}_2\text{CF}_2\text{O}-\text{CHCl}, -\text{CHFCl}, -\text{CFCl};$$
$$\text{CF}_2\text{CF}_2\text{O}-\text{CF}_2\text{CF}_2\text{O}-\text{CHCl}, -\text{CHFCl}, -\text{CFCl};$$
$$\text{CF}_2\text{CF}_2\text{O}-\text{CF}_2\text{CF}_2\text{O}-\text{CHCl}, -\text{CHFCl}, -\text{CFCl};$$
$$\text{CF}_2\text{CF}_2\text{O}-\text{CF}_2\text{CF}_2\text{O}-\text{CHCl}, -\text{CHFCl}, -\text{CFCl};$$
$$\text{CF}_2\text{CF}_2\text{O}-\text{CF}_2\text{CF}_2\text{O}-\text{CHCl}, -\text{CHFCl}, -\text{CFCl};$$
$$\text{CF}_2\text{CF}_2\text{O}-\text{CF}_2\text{CF}_2\text{O}-\text{CHCl}, -\text{CHFCl}, -\text{CFCl};$$
$$\text{CF}_2\text{CF}_2\text{O}-\text{CF}_2\text{CF}_2\text{O}-\text{CHCl}, -\text{CHFCl}, -\text{CFCl};$$
$$\text{CF}_2\text{CF}_2\text{O}-\text{CF}_2\text{CF}_2\text{O}-\text{CHCl}, -\text{CHFCl}, -\text{CFCl};$$
$$\text{CF}_2\text{CF}_2\text{O}-\text{CF}_2\text{CF}_2\text{O}-\text{CHCl}, -\text{CHFCl}, -\text{CFCl};$$
$$\text{CF}_2\text{CF}_2\text{O}-\text{CF}_2\text{CF}_2\text{O}-\text{CHCl}, -\text{CHFCl}, -\text{CFCl};$$
$$\text{CF}_2\text{CF}_2\text{O}-\text{CF}_2\text{CF}_2\text{O}-\text{CHCl}, -\text{CHFCl}, -\text{CFCl};$$
$$\text{CF}_2\text{CF}_2\text{O}-\text{CF}_2\text{CF}_2\text{O}-\text{CHCl}, -\text{CHFCl}, -\text{CFCl};$$
$$\text{CF}_2\text{CF}_2\text{O}-\text{CF}_2\text{CF}_2\text{O}-\text{CHCl}, -\text{CHFCl}, -\text{CFCl};$$
$$\text{CF}_2\text{CF}_2\text{O}-\text{CF}_2\text{CF}_2\text{O}-\text{CHCl}, -\text{CHFCl}, -\text{CFCl};$$
$$\text{CF}_2\text{CF}_2\text{O}-\text{CF}_2\text{CF}_2\text{O}-\text{CHCl}, -\text{CHFCl}, -\text{CFCl};$$
$$\text{CF}_2\text{CF}_2\text{O}-\text{CF}_2\text{CF}_2\text{O}-\text{CHCl}, -\text{CHFCl}, -\text{CFCl};$$
$$\text{CF}_2\text{CF}_2\text{O}-\text{CF}_2\text{CF}_2\text{O}-\text{CHCl}, -\text{CHFCl}, -\text{CFCl};$$

The number average molecular weight of R$''$ being from 66 to 12,000 preferably from 66 to 3,000.
solvents, refrigerants, surfactants, etc. When at least one of \( X_1, X_2, X_3, X_4 \) is equal to \( H \) said products have a low environmental impact.

Furthermore when one operates with a partial fluorination of the starting discyllfluoride and subsequent addition of the formed hypofluorite to a perfluorinated or perfluoroalkyl ether the process of the invention allows to obtain monocarboxylic (per)fluorinated products. (See the Examples.)

When the used olefins contain one or more functional groups as described in 2) and 3), (esters, cyano, amides, —SO\(_2\)-, isocyanates, iso(thio)cyanates, aryIs, optionally substituted, anhydrides, phosphine oxides —PO(O)(C\(_n\)H\(_{2n+1}\)) or phosphonates —P(O\(_2\))(C\(_n\)H\(_{2n+1}\)) the obtained (per)haloether products can be used as surfactant compounds, for treatment of surfaces (oil and water repellents) and additives.

A further object of the present invention is a process for obtaining the formula (I) (per)haloethers, excluding only the case when \( L=0 \) \( X \) is different from \( F \), comprising the following steps:

- synthesis of the formula (II) hypofluorite

\[
X':\text{R}_{2}O—\text{CF}_{2}\text{CF}_{2}—\text{OF}
\]  

wherein:

\( X' \) has the following meanings:

F, linear or branched C\(_{1}\)–C\(_{2}\) per(halo)alkyl preferably perfluoroalkyl, wherein optionally one chlorine atom is substituted with one chlorine atom; or

—[O\(_2\)]\(_{2}\)CF\(_{2}\)CF\(_{2}\)OF, —[O\(_2\)]\(_{2}\)CF\(_{2}\)C(O)\(_{2}\)F, wherein \( n=0 \) when \( RF=RF' \) as above; \( n=1 \) when \( RF=RF' \) as above; \( n=2 \) when

- \( L=0; \)
- \( L=0, 1; \)
- when \( L=0 \) then \( X' \) is different from \( F \) and from —CF\(_{2}—\)
- CF\(_{2}OC\(_{2}\)Me; when \( L=1 \) RF=RF' or RF\(_{2}\); being RF=C\(_{1}\)–C\(_{2}\) perfluoroalkylene and RF\(_{2}\)=perfluoroalkoxyalkylene having formula (V) as above, more preferably having formula (VI) as above, the number average molecular weight of RF\(_{2}\) being from 66 to 12,000;
- when \( L=1 \) and RF=RF' \( X' \) is also C\(_{1}\)–C\(_{2}\) perfluoroalkyl; by fluorination of an acyfluoride of formula (III)

\[
X':\text{R}_{2}O—\text{CF}_{2}—\text{C(O)}\text{F}
\]  

wherein \( X'\), \( L \) and RF have the above meanings, at temperatures between —100° and +50° C., preferably between —80° and +20° C., in the presence of a catalyst, or mixtures of catalysts, having general formula Me\(_{2}\)CH\(_{2}\)Ph; wherein Me is an alkaline or alkaline-earth metal, or silver; \( y \) is 1 or 2, depending on the metal valence, \( z \) is zero or ranges from 0.5 to 4, preferably \( z=0 \) or 1; in absence or in the presence of inert, liquid or gaseous diluents;

b reaction of the hypofluorites (II) with (per)halo-olefins of formula

\[
\text{CX}_{2}\text{X}_{3}:=\text{CX}_{2}\text{X}_{3}
\]  

wherein \( X_1, X_2, X_3, X_4 \) are as above, at a temperature in the range from 0° C. to 120° C., preferably from —60° C. to —110° C., in absence or in the presence of inert, liquid or gaseous diluents.

Examples of olefins that can be used in the process of the present invention are for instance the following:

<table>
<thead>
<tr>
<th>CF(<em>{3})C(</em>{2})H(_{2})</th>
<th>CF(<em>{3})C(</em>{2})H(_{2})</th>
<th>CH(<em>{3})CH(</em>{2})</th>
<th>CH(<em>{3})CH(</em>{2})</th>
<th>CH(<em>{3})CH(</em>{3})</th>
<th>CH(<em>{3})CH(</em>{3})</th>
<th>CH(<em>{3})CH(</em>{3})</th>
<th>CH(<em>{3})CH(</em>{3})</th>
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</thead>
<tbody>
<tr>
<td>CF(<em>{3})C(</em>{2})H(_{2})</td>
<td>CF(<em>{3})C(</em>{2})H(_{2})</td>
<td>CH(<em>{3})CH(</em>{2})</td>
<td>CH(<em>{3})CH(</em>{2})</td>
<td>CH(<em>{3})CH(</em>{3})</td>
<td>CH(<em>{3})CH(</em>{3})</td>
<td>CH(<em>{3})CH(</em>{3})</td>
<td>CH(<em>{3})CH(</em>{3})</td>
</tr>
</tbody>
</table>
acrylic acids, CH₂–CH–O–(O)CH₃; CH₂–CH–
CH₂–O–(O)CH₂CH₃. CH₂–CH–
CN; CH₂–CH–CH₃COOMe,
CH₂–CH–CH₂Cl, dimethyl or diethyl esters of maleic or
fumaric acid, maleic anhydride, itaconic anhydride.
The process according to the present invention can be
 carried out in a discontinuous, semicontinuous or in a contin-
uous way.
The discontinuous and semicontinuous processes imply
the use of a sole reactor, wherein the fluorination and addition
reactions (one pot reactions) are carried out.
When one operates in a discontinuous or semicontinuous
way, in step b) preferably the olefin is added to the hypofluo-
torite.
The continuous process implies the use of two separate
reactors wherein the fluorination and the addition reaction
to the olefin are respectively carried out.
With the processes in a discontinuous, semicontinuous and
continuous way, preferably the hypofluorite concentration
in the added inert, liquid or gaseous diluent, such as for example
those mentioned below, is higher than 50% by weight, pref-
emblu higher than 70% by weight, still more preferably one
works in absence of inert diluent, to avoid the above men-
tioned drawbacks of the prior art.
The fluorination reaction for preparing the hypofluorite
step a) can be carried out in excess or in deficit of fluorine
with respect to the acrylfluoride, at temperatures in the range from
–100° to +50° C., preferably from –80° to +20° C., in absence
or in the presence of a diluent inert under the reaction condi-
tions. The diluents mentioned below, for example C₂F₆, C₃F₈
(eycle), C₂F₆O(eother), CF₃O–(CF₂)₃–CF₃, N₂, CF₃O C₂F₆,
perfluoroalkanes, for example Golden® HT 55, can be
used.
The formula (III) acrylfluorides can be prepared by synthe-
sis of the peroxodic raw product and subsequent reduction
to obtain perfluoropolyether components having end acylflu-
oridaes. The peroxodic raw product synthesis is carried out by
oxidative polymerization of fluoroolefins, in particular C₂F₆
and/or C₃F₈ with oxygen at low temperature, in the presence
of UV light or of a radical initiator, as for example described
in patents GB 1,189,337, GB 1,104,482, U.S. Pat. No. 3,683,
027, U.S. Pat. No. 3,175,378, U.S. Pat. No. 5,149,842, U.S.
Pat. No. 5,258,110, U.S. Pat. No. 5,488,181. The peroxodic
raw product reduction is carried out with hydrogen on a
suitable catalyst containing palladium to give perfluoro-
opolyether products having acylfluoride end groups, for example
as described in U.S. Pat. No. 3,847,978, U.S. Pat. No. 6,127,498.
Alternatively perfluoroalkane products having acylfluoro-
ide end groups can be obtained by fluoroloein photooxida-
tion in the presence of a chain transfer agent as described in
U.S. Pat. No. 5,433,899. Besides U.S. Pat. No. 5,446,514
describes the preparation of oligomers (OCF₂)ₙ having
—OCF₂–COF end groups.
The acrylfluorides are obtainable also by electrochemical
fluorination of the corresponding carbonyl compounds, according
to known methods of the prior art. Said process is applicable
also for the acrylfluorides wherein R=FR.
The catalysts used in step a) are known in the prior art. U.S.
Pat. No. 4,827,024, U.S. Pat. No. 4,499,024, EP 754,670,
pp. 1809–1810 can be mentioned. As an example the follow-
ing can be mentioned: LiF, NaF, KF, CsF, KH₂F₂, AgF. Said
catalysts can be used as such or mixed among each other.
The fluorination reaction can be carried out at a pressure
equal to or higher than the atmospheric pressure, for example
up to 2 atmospheres, and it takes place with very short contact
times. The conversion of the reactant in deflect, with respect to
the equimolar stoichiometry between acrylfluoride equiva-
lets and F₂ fluorine moles, is complete and the hypofluorite
fluorination yield, calculated with respect to the reactant in
defect, is very high, generally higher than 95%.
With inert diluents usable in the present invention process
are meant liquid or gaseous compounds inert under the reac-
tion conditions. In particular inert diluents, also usable in step
b), are for example C₂F₆, C₃F₈, C₃F₆, C₂F₆O (ether), (per)
fluoropolyethers, for example Golden® HT 55 (perfluoro-
opolyether solvent having b.p. 55° C.), α,ω-dihydrofluoro-
opolyethers, preferably the boiling point of the (per)
fluoropolyethers and α,ω-dihydrofluoropolyethers is in the
range from 30° C. to 300° C., CHCl₃–CF₃, CF₃–CH₂F,
CF₂–CF₂Cl.
In the discontinuous process a single addition is made of
the required amount of fluorine to the suspension containing
the catalyst and acrylfluoride, at the above temperatures from
–80° C. to +20° C. The subsequent fluorination reaction takes
place with total conversion of the acrylfluoride. After elimina-
tion of the unreacted fluorine, the (per)haloolefin is added to
the hypofluorite, in absence or in the presence of the above
diluents, at temperatures preferably in the range from –110°
C. to –60° C., to obtain the final (per)haloether component.
In the discontinuous process according to the present inven-
tion the two consecutive reactions of the acrylfluoride fluori-
nation and of the olefin addition to the hypofluorite are car-
ried out in a sole reactor, by alternating the fluorine feeding
with that of the olefin. In the reactor the catalyst based on
fluoride metal necessary in the first fluorination phase is
always present. The catalyst used in the present invention
process is inert under the conditions of the hypofluorite addi-
tion reaction to the (per)halo-olefin. After the last olefin addi-
tion the reaction product is separated from the catalyst and
from the optional reaction solvent, by using known separa-
tion methods, such as for example filtration, distillation or stripping
under vacuum.
The yields of the addition reaction to (per)halo-olefins, also
in absence of diluent, are high, generally in the range 50%–
90% calculated with respect to the hypofluorite.
The semicontinuous process implies that the fluorination
reaction be carried out at the above temperatures, by flowing
gaseous fluorine, optionally diluted with an inert gas such as,
for example, nitrogen, He, CF₃F, CF₂F₂, CF₃CF₂F, in the sus-
pension containing the catalyst and the acrylfluoride, until
obtaining an acrylfluoride conversion percentage from 1% to
80%, preferably from 5% to 60%. The fluorine conversion is
complete. When the fluorine addition is over, the (per)halo-
olefin is added to the suspension containing the hypofluo-
rite, the catalyst and the unreacted acrylfluoride, at a tempera-
ture from 0° C. to –120° C., preferably from –60° C. to –110°
C., until to a complete hypofluorite conversion. The olefin can
be added as such or dispersed in a liquid or gaseous diluent,
selected from those above mentioned for the addition reac-
tion. When the olefin addition is ended, one proceeds with a
further fluorination reaction with conversion of other
acylfluoride to hypofluorite, followed by a second addition
of olefin. The sequence of the fluorination and addition reac-
tions is repeated until obtaining the complete acrylfluoride
conversion. The addition yields to the (per)haloolefins, also in
absence of the inert diluent, are very high, generally in the
range 50%–90% calculated with respect to the hypofluorite.
The advantage of the semicontinuous process resides in
that a sole reactor is used, eliminating the hypofluorite trans-
fer from the fluorination reactor to that in which the addition
reaction takes place, which as said can give rise to decomposition phenomena. Also in absence of reaction solvent the addition yields are high.

In the continuous process two separate reactors are used. In the first reactor (reactor 1) the acyl fluoride fluorination reaction takes place; in the second reactor (reactor 2) the addition to the (per)halo-olefin. In the fluorination the conversion of the reactant in defect is complete with respect to the equimolar ratio between acyl fluoride equivalents and fluorne moles. The hypofluorite fluorination yield, calculated with respect to the reactant in defect, is very high, generally higher than 95%.

When in the fluorination step a) of the continuous process the reactant in defect is fluorine, the reaction is preferably carried out in absence of diluents, both liquid and gaseous; when the reactant in defect is the acylfluoride (fluorine in excess), or when the reactants are introduced in stoichiometric amounts, it is preferred to operate in the presence of an inert diluent, selected for example from those above indicated for the fluorination reaction.

The formed hypofluorite, and the optional unreacted acylfluoride are fed to the reactor 2. In the latter reactor, besides the mixture containing hypofluorite and acylfluoride, the (per)halo-olefin is introduced in a continuous way at the pure state, or diluted with a suitable inert, gaseous or liquid diluent, selected from those indicated above for the addition reaction.

In step b) of the continuous process the ratio between the equivalents of hypofluorite/hour (eq.-OF/h) and the equivalents of olefin/hour (eq.-olefin/h) which are contemporaneously introduced into the addition reactor is from 0.5 to 2.0, preferably from 0.8 to 1.2.

The reaction raw product, containing the unreacted acylfluorides and the addition product, is continuously recovered from the bottom of the reactor 2 and fed to the fluorination reactor 1 wherein the still present acylfluorides are fluorinated to hypofluorites with elemental fluorine, then fed again to the addition reactor.

With the continuous process the complete acylfluoride conversion is collected in the corresponding (per)halo-ether is obtained. It is collected as liquid in the addition reactor and optionally purified by simple distillation.

Even in absence of inert diluents, the addition yields of hypofluorites to (per)halo-olefins, calculated with respect to the hypofluorite, are very high, generally in the range 50%-90%.

In the continuous process one preferably operates in step a) with fluorine in defect, still more preferably in absence of inert diluents, with very good productivity of the (per)haloethers. In particular said result is obtained also by using hypofluorites having a high boiling point.

The reaction solvent absence allows to obtain the following advantages:
- to eliminate the environmental dangers connected to the solvent use;
- to recover the reaction products avoiding high distillation volumes;
- to reduce the plant operating costs.

The present invention process comprising the hypofluorite synthesis and the addition reaction with (per)halo-olefins is particularly advantageous for the hypofluorites having a boiling point higher than –10°C.

As it has been seen, in the prior art using said hypofluorites for obtaining (per)haloethers, it is difficult to avoid partial or total condensation phenomena of hypofluorites, in correspondence of which, as said, very exothermic undesired decomposition reactions can take place, reducing drastically the (per)haloethers yields.

A further object of the present invention are hypofluorites of formula (II), wherein Rf=as defined, X' has the following meanings:
- F, linear or branched C₁₋₃ per(halo)alkyl; preferably per-fluoroalkyl, wherein optionally one fluorine atom is substituted with one chlorine atom; or
- [O₁₋₃ CF₂]OF,

wherein I=0 when Rf=Rf⁺ as above defined; T=1 when R⁻=R⁻ as above.

The preferred hypofluorites are the following:

CF₃OCF₂OCF₂CF₂OF,
CF₃OCF₂OCF₂OFCF₂OF,
CF₃OCF₂OCF₂OCF₂OF,
CF₃OCF₂OCF₂OCF₂OF,
CF₃OCF₂OCF₂OCF₂OF,
CF₃OCF₂OCF₂OCF₂OF,

FOCF₂OCF₂OCF₂OF,
FOCF₂OCF₂OCF₂OCF₂OF,
FOCF₂OCF₂OCF₂OCF₂OF,
FOCF₂OCF₂OCF₂OCF₂OF,

As said, the hypofluorites of the present invention, used according to the above process, allow to obtain high yields in (per)haloether products by addition to (per)halo-olefins.

This is surprising since hypofluorites having a different structure, for example having the carbon atom in beta position with respect to the hypofluorite oxygen substituted with a CF₃ group, or having the hypofluorite oxygen linked to a linear perfluoroalkyl chain with at least three carbon atoms, react with (per)halo-olefins with very low yields in the addition products (see comparative Examples). It is furthermore surprising that the present invention hypofluorites, which can also have a number of carbon atoms in the chain higher than two, are capable to react with the fluoroolefins with good yields, contrary to the teachings of the prior art.

The following Examples illustrate the invention without limiting the purpose thereof.

**EXAMPLE 1**

**Preparation of the CsF Catalyst**

The CsF catalyst, finely milled in an inert atmosphere, is fed to the reactor and dried under a gas stream inert at the temperature of 200°C-250°C for two hours. The so-anhydried catalyst is subsequently fluorinated at 400 mbar (4x10⁻⁶ Pa) of fluorine at the temperature of 150°C for 2 hours, then the fluorine is stripped under vacuum before being used.

**EXAMPLE 2**

Test in a discontinuous way according to the invention process carrying out the synthesis of the bis-hypofluorite of formula FOCF₂CF₂O—(CF₂CF₂O)n(CF₂O)m—CF₂CF₂OF (1) by using the CsF catalyst and fluorine in excess with respect to the starting acylfluoride.

0.90 g of CsF catalyst prepared as described in Example 1 are introduced in a 10 ml metal reactor, equipped with internal thermocouple.

Then by operating under inert atmosphere (dry-box) 2 mmoles of diacylfluoride of formula

FO(CF₂O)n(CF₂CF₂O)m—CF₂CF₂OF

having number average MW 460 are introduced; m/n=4.50 and having a functionality in —COF end groups 1.82 and functionality in —CF₃ and end groups 0.18, prepared as from the method described in U.S. Pat. No. 5,258,110 and U.S. Pat. No. 3,847,978.
After cooling in liquid nitrogen, and removal by stripping of the possible uncondensables products under vacuum, 5.47 mmol of fluorine are added. The reaction mixture is brought to ~10° C, and it is left for 4 hours. It is cooled at ~196° C and 1.70 mmol of unreacted F₂ is recovered and eliminated. The reaction mixture is brought to ~105° C, and after having condensed 3 mmol of perfluoropropane (C₃F₈), 5.47 mmol of CFCI═CFCI are slowly added maintaining the temperature at ~105° C. When the addition is over, the reaction mixture is left at ~105° C. for 1 hour, then brought to the temperature of ~70° C. The volatile products are removed by water pump and the reaction mixture is recovered in C₆F₁₄. The ¹³F-NMR and GC/MS analyses show the complete disappearance of the initial —COF₂ end groups.

The absence of the starting acylchlorides in the final reaction mixture, besides confirming the fluorine balance obtained in the fluorination, shows that under these experimental conditions the acylchloride conversion into the corresponding hypofluorite is quantitative.

The formed hypofluorite has the following formula:

\[ FOCF₂CF₂O→(CF₂CF₂O)ₙCF₂CF₂OF \]  (1)

wherein m and n are as above defined.

On the basis of the analysis, at the end of the process the formed perfluoropolyether compounds have the following end groups:

- OCF₂CF₂Cl, deriving from the reaction of the olefin CFCI═CFCI with the end —OF functions of the hypofluorite of formula (1), with 85% yield with respect to the mole of the initial acylchloride;
- OCF₃, deriving from the decomposition of the —CF₂CF₂OF end groups of the hypofluorite (1), with contemporaneous formation of COF₂. Yield of —OCF₃ end groups: 17%, calculated as above.

By GC/MS and GC analyses the following products have also been identified and quantified in the mixture of the reaction products (as % molar):

- CFCI═CF₂CF₂O→(CF₂CF₂O)ₙCF₂CF₂OF: 79%;
- CF₂O→(CF₂CF₂O)ₙCF₂CF₂OF: 27%;
- CF₂O→(CF₂CF₂O)ₙCF₂CF₂OF: 3%.

The reaction products are separated by fractional distillation.

Characterization:

¹³F-NMR of the reaction mixture:

- ¹³F-NMR spectrum in ppm with respect to CFCI₃ on the mixture (ppm=0):
  - ~51.7, ~55.3 (2F —OCF₂O—);
  - ~56.2 (3F C F₂OCF₂CF₂O—);
  - ~57.8 (3F CF₂OCF₂CF₂O—);
  - ~71.0 (2F —CF₂Cl);
  - ~76.5 (1F —CF₂Cl);
  - ~87.5 (3F CF₂CF₂O—);
  - ~88.4, ~90.7 (4F —OCF₂CF₂O—).

Example 2 has been summarized in Table 1.

EXAMPLES 2A-2C

Likewise Example 2, the Examples 2A and 2C have been performed and have been summarized in Table 1.

EXAMPLES 3-3B

In these Examples, which have been summarized in Table 1, the process according to the present invention is carried out starting from a diacylfluoride having a higher molecular weight, homologue of that used in Example 2 and prepared according to patents mentioned therein, having the following characteristics: molecular weight 620, m/n = 4.30, functionality in —COF end groups: 1.82, functionality in —CF₂CF₂ end groups: 0.18.

The fluorination and addition reactions of the olefin are substantially carried out as described in Example 2.

Table 1 shows that by operating in excess of fluorine, as in the Examples 2A-2C and 3-3B, the conversion of diacylfluoride into bis-hypo-fluorite is quantitative and the olefin addition yields are high.

EXAMPLE 4

Test in a discontinuous way according to the invention wherein the synthesis of the bis-hypo-fluorite (1) is carried out by partial fluorination of the corresponding dia-cyfluoride on CsF catalyst.

2 mmol of diacylfluoride of formula

\[ F(O)CF₂CF₂O→(CF₂CF₂O)ₙCF₂CF₂OF \]

having number average MW 620 are introduced in a 10 ml metal reactor, equipped with internal thermocouple containing the CsF catalyst (0.90 g), by operating likewise as in Example 2; m/n = 4.30, functionality in —COF end groups 1.82, functionality in —CF₂CF₂ end groups 0.18, prepared as indicated in patents reported in Example 2.

After cooling in liquid nitrogen, the possible uncondensables products stripped, 2.50 mmol of fluorine are added and the reaction mixture is left at ~10° C. for 4 hours. At the end of the fluorination it is found that the fluorine conversion is complete.

At the temperature of ~105° C., after having condensed 3 mmol of perfluoropropane (C₆F₁₄), 3.5 mmol of CFCI═CFCI are slowly added. When the addition is over, the reaction mixture is left at ~105° C. for 1 hour, then brought to the temperature of ~70° C. The volatile products are removed by water pump.

The reaction products are then recovered in C₆F₁₄. The ¹³F-NMR analysis shows that the conversion of the initial —COF₂ end groups is 69%.

The amount of each type of end group formed, calculated in % by moles with respect to the converted diacylfluoride, is respectively the following:

- OCF₂CF₂Cl: 62%;
- OCF₃: 38%.

Example 4 is summarized in Table 1.

By the GC/MS and GC analyses it is shown that the reaction mixture is formed, besides the starting acylchlorides, which represent 27% by moles with respect to the initial moles, also by the following reaction products, in the indicated percentages, likewise calculated:
The reaction products a), b), c) have been obtained, similarly to the products of Example 2, by addition of the olefin CFCl—CFCl to the corresponding bis-halofluorides of formula (1) (see Example 2); the products d) and e) derive from the addition of the olefin to the corresponding mono-halo-

The quantitative gas chromatographic analysis of all said products has shown that in the partial fluorination reaction of the diacylfluorides the selectivity is the following:

<table>
<thead>
<tr>
<th>bis-halo-fluorides (1)</th>
<th>65%</th>
</tr>
</thead>
<tbody>
<tr>
<td>mono-halo-fluorides (2)</td>
<td>8%</td>
</tr>
<tr>
<td>diacylfluorides</td>
<td>27%</td>
</tr>
</tbody>
</table>

The Example shows that under said experimental conditions the fluorination reaction of diacylfluorides in the presence of the CsF catalyst, even by operating with lower fluo-

The reaction products are separated by fractional distillation.

19F-NMR spectrum in ppm with respect to CFCl3 on the mixture (ppm=0):

13.2 (1F F(OCCF2OCF2OCl)); 13.0 (1F F(OCCF2OCF2OCl)); -51.7, -55.3 (2F OCF2ClO); -56.2 (3F2 OCF2OCF2OCl); -71.0 (2F OCF2ClO); -76.5 (1F CFClO); -77.0 (2F OCF2OCF2OCl); -78.8 (2F OCF2OCF2OCl); -87.5 (3F CF2OCF2OCl); -88.4, -90.7 (4F OCF2OCF2OCl).

EXAMPLE 4A

Test in a discontinuous way according to the invention process wherein the synthesis of the bis-halo-fluoride (1) and mono-halo-fluoride (2) is carried out by partial fluorination of the corresponding diacylfluoride on CsF catalyst.

2 mmole of the diacylfluoride used in Example 4 are fed in a 10 ml metal reactor equipped with internal thermocouple containing the CsF catalyst (0.90 g), by operating likewise as in Example 2.

After cooling in liquid nitrogen, the possible uncondensable products stripped, 2.0 mmole of fluoride are added and the reaction mixture is left at -10°C for 4 hours. At the end of the fluorination it is found that the fluoride conversion is complete. 2.80 mmole of CF3=CF2 are slowly added in the same reactor, brought to the temperature of -105°C, after having condensed 3 mmole of perfluoropropane (CF3F).

When the addition is over, the reaction mixture is then left at -105°C for 1 hour, then brought to the temperature of 70°C, the volatile products are removed by water pump.

The reaction products are then recovered in CF3F. The 19F-NMR analysis shows that the conversion of the initial —COF end groups is 55%. The amount of each end group formed, calculated as % by moles with respect to the converted diacylfluoride, is respectively the following:

| —OCF2CF3 | 32% |
| —OCF2Cl | 68% |

The GC/MS and GC analyses have shown that the following reaction products are formed: monoacylfluorides and neutral perfluoropolyethers, besides the starting unreacted diacylfluorides which represent the 39% by moles with respect to the initial ones, in the following relative molar percentages, determined by gaschromatography:

monoacylfluorides:

| CF3CF2O—CF2CF2OCl | 6% |
| CF3CF2Cl | 13% |

neutral perfluoropolyethers:

| CF3CF2O—CF2CF2OCl | 11% |
| CF3CF2Cl | 21% |

The reaction products are separated by fractional distillation.

Characterization of the products: 19F-NMR

19F-NMR spectrum in p.p.m. with respect to CFCl3 (p.p.m.-0): 13.2 (1F F(OCCF2OCF2OCl)); 13.0 (1F F(OCCF2OCF2OCl)); -51.7, -55.3 (2F OCF2ClO); -56.2 (3F2 OCF2OCF2OCl); -71.0 (2F OCF2ClO); -76.5 (1F CFClO); -77.0 (2F OCF2OCF2OCl); -78.8 (2F OCF2OCF2OCl); -87.5 (3F CF2OCF2OCl); -88.4, -90.7 (4F OCF2OCF2OCl).

The conditions used in this Example and the obtained results are summarized in Table 1A.

EXAMPLES 4B AND 4C

Test in a discontinuous way according to the invention process wherein the synthesis of the bis-halo-fluoride (1) and mono-halo-fluoride (2) is carried out by partial fluorination of the corresponding diacylfluoride on CsF catalyst.

Example 4B is carried out likewise as in Example 4A but by starting from diacylfluoride having number average molecular weight 600 described in Example 2.

Example 4C is carried out likewise as in Example 4 by starting from the diacylfluoride having number average molecular weight 620 but fluorinating the compound at a temperature of +20°C for 4 hours.

The obtained results are shown in Table 1A.

EXAMPLE 5

Test in a discontinuous way according to the invention process wherein in the fluorination a mixture of bis-hypo-
fluorite (1) and mono-hypofoirite F(O)CF_2O—
(CF_2CF_2O)m(CF_2O)n—CF_2CF_2OF (2) is obtained by partial
fluorination of the corresponding diaicy fluoride on KHF_2
catalyst.

3.4 g of KHF_2 catalyst (43 mmole; Aldrich® Chemical Co.) are introduced in a 10 ml metal reactor, equipped with
internal thermocouple and subsequently fluorinated at 400 mbar of fluorine at room temperature for 2 hours.

After fluorine removal by stripping at -196°C, by operating under inert atmosphere (dry-box), 1.90 mmole of dia-
cy fluoride (2-A) are introduced, as in Example 2.

After cooling in liquid nitrogen, the possible uncondens-
able products stripped, 2.80 mmole of fluorine are added and the reaction mixture is left at -10°C. for 5 hours. At the end of the fluorination it is noticed that the fluoride conversion is complete. At the temperature of -105°C, after having condensed 3 mmole of perfluoropropane (C_3F_8), 3.15 mmole of CFCF—CFCl are slowly added.

The reaction mixture is then at -105°C. For 1 hour and subsequently brought to the temperature of -70°C. The volatile products are removed by water pump.

The reaction mixture is then recovered in C_3F_8. The \(^{19F}\) NMR analysis shows that the conversion of the initial —COF end groups is 80%.

The amount of each type of end group formed, calculated in % by moles with respect to the converted diaicy fluoride, is respectively the following:

- OCF(CF_2Cl) 73%;
- OCF_3 27%.

By the GC/MS and GC analyses it is shown that the reaction mixture is formed, besides by the starting diaicy fluoro-
ides, which represents 4% by moles with respect to the initial moles, also by the following reaction products, in the indicated percentages, likewise calculated:

a) CICF_3OCF(CF_2O)m(CF_2O)n—CF_2CF_2OF(CFCFCl) 38%;
b) CICF_3OCF(CF_2O)m(CF_2O)n—CF_2CF_2OF(CFCFCl)
   14%;
c) CICF_3OCF(CF_2O)m(CF_2O)n—CF_3 12%;
d) F(O)OCF(CF_2O)m(CF_2O)n—CF_2CF_2OCF(CFCFCl) 26%;
e) F(O)OCF(CF_2O)m(CF_2O)n—CF_3 6%.

The reaction products a), b), c), d) and e) have been obtained, similarly to the products of Example 2, by addition of the olefin CICFCl—CFCl to the corresponding bis-hypofoirites (1); the products d) and e) derive from the addition of the olefin to the corresponding mono-hypofoirites (2) (Example 4).

The quantitative gaschromatographic analysis of all said products has shown that in the fluorination reaction, by using the KHF_2 catalyst, the selectivity for each product which is in the reacted mixture is the following:

<table>
<thead>
<tr>
<th>Product</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>bis-hypofoirites (1)</td>
<td>64%</td>
</tr>
<tr>
<td>mono-hypofoirites (2)</td>
<td>32%</td>
</tr>
<tr>
<td>diaicy fluoride</td>
<td>4%</td>
</tr>
</tbody>
</table>

In particular for the addition reaction of the olefin CICFCl—CFCl to the mono-hypofoirites (2), it has been found that the yield in —OCF(CF_2Cl) end groups is 81%, and the yield in —OCF_3 end groups is 19%, calculated on the moles of the formed monohypofoirites.

The reaction products are separated by fractional distilla-
tion.

19F-NMR spectrum in ppm with respect to CFCl_3 of the mixture (ppm):
- 13.2 (1F F(O)OCF(CF_2O)m(CF_2O)n—CF_2CF_2OF(Cl)); 13.0 (1F F(O)OCF(CF_2O)_m(CF_2O)n—CF_2CF_2OF(Cl)); -51.7, -55.3 (2F —OCF_2O—CF_2CF_2OF(Cl)); -55.6 (3F CF_3OCF(CF_2O)_n—CF_2CF_2OF(Cl)); -75.8 (3F CF_3OCF_2OF(Cl)); -71.0 (2F —CF_3CF_3); -76.5 (1F —CF_3CF_3); -77.0 (2F —CF_3CF_3OF(COF)); -78.8 (2F —OCF_2OF(COF)); -87.5 (3F CF_3CF_2OF(Cl)); -88.4, -90.7 (4F —OCF_3CF_2OF(Cl)).

Example 5 is summarized in Table 2.

Example 6 has been carried out as Example 5 but by using in the fluorination reaction a diaicy fluoride similar to that used in Examples 3-3B, having molecular weight 620, m/n=4.30, functionality in —COF end groups=1.82, functionality in —CF_3 end groups=0.18.

The Example has been summarized in Table 2.

Table 2 shows that the fluoride conversion under the used experimental conditions is substantially quantitative independently from the molecular weight of the diaicy fluoride. The addition yields of monohypofoirites (2), similarly to those of the bis-hypofoirites (1), are very high.

Example 7

Test in a semi-continuous way according to the invention process with synthesis of the bis-hypofoirite (1) carried out by fluorination in fluorine excess of the corresponding diaicy fluoride on CsF catalyst.

0.90 g of CsF catalyst are introduced in a 10 ml metal jacket, equipped with internal thermocouple and subsequently activated as per Example 1.

After fluorine removal by operating under inert atmosphere (dry-box) 2 mmole of diaicy fluoride used in the Examples 3-3B are introduced. After cooling in liquid nitrogen, the possible uncondensable products stripped under vacuum, 1.83 mmole of fluorine are added. After the reaction mixture has been brought to -10°C, it is let react for 2 hours obtaining the complete disappearance of the fed fluorine. The reaction mixture is brought to -105°C. and after having condensed 3 mmole of perfluoropropane (C_3F_8), 1.0 mmole of CICF—CFCl are slowly added, maintaining the temperature at -105°C.

When the addition is over, the reaction mixture is left at -105°C. For 1 hour and then the fluorination and olefin addition reactions are repeated as described hereinafter.

The reaction mixture is brought to the temperature of -196°C. 3.67 mmole of fluorine are added, the temperature is increased to -10°C. maintaining the reaction mixture under said conditions for 2 hours. It is cooled again to -196°C. and 0.67 mmole of unreacted F_2 are recovered, which is removed by stripping. The temperature is brought to -105°C. and 5.47 mmole of CICF—CFCl are slowly added.

The temperature is maintained at -105°C. For 1 hour and then it is increased to -70°C., removing the volatile products by water pump.

The reaction mixture is then recovered in C_3F_8 and analyzed by \(^{19F}\) NMR analysis. The diaicy fluoride conversion is 90%.
The amount of each type of end group formed, calculated in % by moles with respect to the converted diacylfuride, is respectively the following:

\[ -
\text{OCF}_3/C\text{CF}_3\text{Cl}: 62\%
\]

The main reaction products of the addition of the olefin CFCI=CFCI to the bis-hydrofluorite (1) have been identified and quantified by GC/MS and GC analyses.

Said products are equal, respectively, to the products a), b) and c) obtained in Example 2. The selectivity is comparable to that obtained in Example 2.

The reaction products are separated by fractional distillation.

The product characterization by \(^{19}F\)-NMR is equal to that reported in Example 2.

**EXA\-\text{MPL} 8**

Comparative

**Synthesis of the Perfluoroalkyl Hypohfluorite**

C\(\text{F}_3\text{C}_{2}\text{F}_2\text{OF} \) and Addition to the Olefin CFCI=CFCI

0.90 g of CsF catalyst, prepared as described in Example 1, are introduced in a 10 ml metal reactor, equipped with internal thermocouple, and 2 mmol of C\(\text{F}_3\text{C}_{2}\text{F}_2\text{OF} \) is obtained as in Example 7 of U.S. Pat. No. 4,769,184, and 4 mmol of fluorine are condensed on the catalyst. It is heated at \(-80^\circ\text{C}\) for 4 hours. After cooling in liquid nitrogen, 2 mmol of unreacted fluorine are recovered, obtaining an acylfluoride conversion of 100%.

After removal of the fluorine in excess by stripping, the obtained hypohfluorite C\(\text{F}_3\text{C}_{2}\text{F}_2\text{OF} \) is slowly added, at the temperature of \(-105^\circ\text{C}\), in a 25 ml glass reactor, equipped with magnetic stirrer and internal thermocouple, wherein 6 mmol of CFCI=CFCI and 12 mmol of CFCI, were previously condensed. When the addition is over, the reaction mixture is left at \(-105^\circ\text{C}\) for 1 hour. The \(^{19}F\)-NMR and GC/MS analyses on the reaction mixture have shown the complete disappearance of the initial acylfluoride C\(\text{F}_3\text{C}_{2}\text{C}2\text{F}_3\text{O} \) to mainly give the COF\(_2\), C\( \text{F}_3\text{C}_{2}\text{F}_2\text{OF} \) degradation products, and, in a small part, with a yield by moles of 4% with respect to the initial acylfluoride, the addition product to the olefin having formula C\(\text{F}_3\text{C}_{2}\text{F}_2\text{C}_{2}\text{F}6\text{OF} \). This example shows that hypohfluorites having a linear sequence of carbon atoms equal to or higher than 3 sum the olefins with very low yields.

**EXA\-\text{MPL} 9**

Comparative

**Synthesis of the Hypfluorite C\(\text{F}_3\text{O}([\text{C\(\text{F}_3\text{CF}_3\text{OF}\text{]}\text{]}\text{]} \) and Addition to the Olefin CFCI=CFCI (Comparative Test)**

0.90 g of CsF catalyst, prepared as described in Example 1, are introduced in a 10 ml metal reactor, equipped with internal thermocouple, and 2 mmol of the acylfluoride of formula C\(\text{F}_3\text{O}([\text{C\(\text{F}_3\text{CF}_3\text{OF}\text{]}\text{]}\text{]} \) is obtained as in Example IV of U.S. Pat. No. 5,114,778, and 4 mmol of fluorine are condensed on the catalyst. It is heated at \(-80^\circ\text{C}\) for 4 hours. After cooling in liquid nitrogen, 1.6 mmol of unreacted fluorine are recovered. After removal of the fluorine in excess by stripping, the obtained hypohfluorite C\(\text{F}_3\text{O}([\text{C\(\text{F}_3\text{CF}_3\text{OF}\text{]}\text{]}\text{]} \) is slowly added, at the temperature of \(-80^\circ\text{C}\), in a 25 ml glass reactor, equipped with magnetic stirrer and internal thermocouple, wherein 6 mmol of CFCI=CFCI and 12 mmol of CFCI, were previously condensed.

When the addition is over, the reaction mixture is left at \(-80^\circ\text{C}\) for 1 hour. The \(^{19}F\)-NMR and GC/MS analyses on the reaction mixture have shown a conversion of 93% of the initial acylfluoride C\(\text{F}_3\text{O}([\text{C\(\text{F}_3\text{CF}_3\text{OF}\text{]}\text{]}\text{]} \) to give the COF\(_2\), C\( \text{F}_3\text{C}_{2}\text{F}_2\text{OF} \), C\( \text{F}_3\text{O}([\text{C\(\text{F}_3\text{CF}_3\text{OF}\text{]}\text{]}\text{]} \) products deriving from the hypohfluoride degradation and, in a small part, with a yield of 2% with respect to the initial acylfluoride, the addition product of the hypohfluorite to the olefin having formula C\(\text{F}_3\text{O}([\text{C\(\text{F}_3\text{CF}_3\text{OF}\text{]}\text{]}\text{]} \). This example shows that hypohfluorites having a linear sequence of carbon atoms equal to or higher than 3 sum the olefins with very low yields.

**EXA\-\text{MPL} 10**

Test in a discontinuous way according to the invention process carrying out the synthesis of the bis-hypohfluorite of formula F\(\text{O}([\text{C\(\text{F}_3\text{CF}_3\text{OF}\text{]}\text{]}\text{]} \) is obtained as in Example IV of U.S. Pat. No. 5,114,778, and 4 mmol of fluorine are condensed on the catalyst. It is heated at \(-80^\circ\text{C}\) for 4 hours. After cooling in liquid nitrogen, 1.6 mmol of unreacted fluorine are recovered. After removal of the fluorine in excess by stripping, the obtained hypohfluorite F\(\text{O}([\text{C\(\text{F}_3\text{CF}_3\text{OF}\text{]}\text{]}\text{]} \) is slowly added, at the temperature of \(-80^\circ\text{C}\), in a 25 ml glass reactor, equipped with magnetic stirrer and internal thermocouple, wherein 6 mmol of CFCI=CFCI and 12 mmol of CFCI, were previously condensed.

When the addition is over, the reaction mixture is left at \(-80^\circ\text{C}\) for 1 hour. The \(^{19}F\)-NMR and GC/MS analyses on the reaction mixture have shown a conversion of 93% of the initial acylfluoride F\(\text{O}([\text{C\(\text{F}_3\text{CF}_3\text{OF}\text{]}\text{]}\text{]} \) to give the COF\(_2\), C\( \text{F}_3\text{C}_{2}\text{F}_2\text{OF} \), C\( \text{F}_3\text{O}([\text{C\(\text{F}_3\text{CF}_3\text{OF}\text{]}\text{]}\text{]} \) products deriving from the hypohfluoride degradation and, in a small part, with a yield of 2% with respect to the initial acylfluoride, the addition product of the hypohfluorite to the olefin having formula C\(\text{F}_3\text{O}([\text{C\(\text{F}_3\text{CF}_3\text{OF}\text{]}\text{]}\text{]} \). This example shows that hypohfluorites having a linear sequence of carbon atoms equal to or higher than 3 sum the olefins with very low yields.
The products are separated by fractional distillation.

19F-NMR spectrum in p.m.m. with respect to CFCI₃ (p.m.m.: 0) : -51.7, -55.3 (2F —OCF₂CF₂O—); -56.2 (3F C F₃OCF₂CF₂O—); -57.8 (3F C F₃OOCF₂O—); -87.5 (3F C F₃OCF₂O—); 59.8, -90.7 (4F —OCF₂CF₂O—); -91.1, 59.18 (2F —OCF₂CF₂OCHCICHFCI); -143.4, -145.2 (1F —OCF₂CF₂OCHCICHFCI).

EXAMPLES 10A-10E

These Examples have been carried out likewise as in Example 10, except for the following differences:

In Example 10D the ethyl acrylate olefin (4.37 mmoles) has been added in the reactor at the temperature of -196°C, and the reaction mixture has been kept at the temperature of -50°C, then left at this temperature for one hour.

In Example 10E the maleic anhydride olefin (4.37 mmoles) dissolved in acetonitrile (2 ml) has been added to the reactor at the temperature of -196°C, and the reaction mixture has been kept at the temperature of -30°C, and left at this temperature for one hour.

The obtained results have been summarized in Table 3.

EXAMPLE 11

Test in a discontinuous way according to the invention process wherein the synthesis of the bis-hypofluorite (1) and mono-hypofluorite (2) is carried out by partial fluorination of the corresponding diacyl fluoride on CsF catalyst and addition to CF₃O—CF₃

2 mmoles of diacyl fluoride F(OCOCF₂O—(CF₃CF₂O)n (CF₃O)—CF₃)OF used in Examples 4 and 3B, are introduced in a 10 ml metal reactor equipped with internal thermocouple and containing the CsF catalyst (0.90 g), by operating likewise as in Example 4.

After cooling in liquid nitrogen, the possible uncondensable products stripped, 2.10 mmoles of fluorine are added and the reaction mixture is left at -10°C for 4 hours. At the end of the fluorination it is found that the fluorine conversion is complete. At the temperature of -80°C, after having condensed the reaction 3 mmoles of A-11 (CFCI₃), 2.80 mmoles of trans-1,2-dichloroethylene are slowly added. When the addition is over, the reaction mixture is then left at -80°C for one h, then brought to -50°C, and the volatile products are removed by water pump.

The reaction products are then recovered in C₆F₆.

The 19F-NMR analysis shows that the conversion of the initial —COF end groups is 49% to give products having the following neutral end groups in the molar percentages indicated below, calculated with respect to the converted —COF:

| —OCF₂CF₂O₃ | 90% |
| —OCF(CF₃)O₃ | 10% |

The products are separated by fractional distillation.

19F-NMR spectrum in p.m.m. with respect to CFCI₃ (p.m.m.: 0) : 13.2 (1F F(OCOCF₂O)—); 13.0 (1F F(OCOCF₂O CF₂O)—); -51.7, -55.3 (2F —OCF₂O —); -55.4 (3F CF₃OOCF₂O—); -56.2 (3F CF₃OOCF₂O—); -57.8 (3F CF₃OCF₂O—); -77.0 (2F CF₃OCF₂O—CF₃C(O)F); -78.8 (2F CF₃OCF₂O—CF₃C(O)F); -86.7 (3F —OCF(CF₃)OCF₂O—); -87.5 (3F C F₃CF₂O—); -88.4, -90.7 (4F —OCF₂CF₂O—); -98.2 (1F —OCF(CF₃)OCHCICHFCI).

EXAMPLE 12

Test in a discontinuous way according to the invention process wherein the synthesis of the bis-hypofluorite (1) and mono-hypofluorite (2) is carried out by partial fluorination of the corresponding diacyl fluoride on CsF catalyst and addition to CF₃O—CF₃

2 mmoles of diacyl fluoride F(OCOCF₂O—(CF₃CF₂O)n CF₃O—CF₃C(O)F of Example 4 are introduced in a 10 ml metal reactor equipped with internal thermocouple containing the CsF catalyst (0.90 g), by operating likewise as in Example 11.

After cooling in liquid nitrogen, the possible uncondensable products stripped, 1.82 mmoles of fluorine are added and the reaction mixture is left at -10°C for 4 hours. At the end of the fluorination it is found that the fluorine conversion is complete. The reaction mixture is brought to -105°C and after having condensed 3 mmoles of perfluoropropane (C₃F₈), 2.80 mmoles of CF₃OCF₂O—CF₃ are added.

When the addition is over, the reaction mixture is then left at -105°C for one h, then brought to -70°C, and the volatile products are removed by water pump.

The reaction products are then recovered in C₆F₆.

The 19F-NMR analysis shows that the conversion of the initial —COF end groups is 49% to give products having the following neutral end groups in the molar percentages indicated below, calculated with respect to the converted —COF:

| —OCF₂CF₂O₃ | 51% |
| —OCF₄ | 49% |
EXAMPLE 13

Test in a semicontinuous way according to the invention process wherein the synthesis of the bis-hypofluorite (1) is carried out by fluorination of the corresponding diacylfluoride on CsF catalyst and addition to CFCI—CFCl
2.3 g of CsF catalyst, which is activated by heating at 200° C. for 4 hours in an inert atmosphere and then subsequently fluorinated with 1 Nl/h of F₂, diluted with 1 Nl/h of He at the temperature of 150° C. for 4 hours, are introduced in a 420 ml metal reactor equipped with reflux condenser, mechanical stirrer and internal thermocouple.

After removal of the residual fluorine, 100 g (0.22 moles) of the diacylfluoride (MW=460) of Example 2 are fed, then the reaction mixture is brought to −80° C. by an external cryostat. A mixture formed by 1.0 litres/h (1/h) of elementary fluorine diluted with 0.5 litres/h of helium is flushed into the reactor for 1 hour. The gas chromatographic analyses of the gases outflowing from the reactor show how the fluorine yield with respect to the fed fluorine is 95%.

Then the reaction mixture is brought to −105° C. by an external liquid nitrogen cryogenic system and a mixture formed by 1 Nl/h of CFCI—CFCl diluted with 4 Nl/h of He is added at the temperature of −105° C. in one hour.

The reaction mixture is brought again to −80° C. where one proceeds to a further fluorination and subsequently to a further addition of olefin, under the same above mentioned conditions. The reaction is followed by 19F-NMR analysis up to the complete conversion of the initial —COF end groups. With the sequence of the described operations a total fluorine amount of 0.42 moles is introduced with a fluorine yield of 95%.

When the reaction is over, the formed products, separated from the catalyst, are analyzed by 19F-NMR analysis.

The conversion of the starting acylfluoride is quantitative.

The amount of each end group formed, expressed in % by moles with respect to the converted diacylfluoride, is respectively the following:

| —OCFCCFCl | 85% |
| —OF₂ | 15% |

By GC/MS and GC analysis it is shown that the reaction mixture is formed by the following reaction products in the indicated molar percentages:

a) CCl₅F₂OCFCCFCO(CF₅O)₅—CCl₅F₂OFCCFCF₅Cl —72%

b) CCl₅F₂OCFCCFCO(CF₅O)₅—CCl₅F₂OFCCFCF₅Cl —26%

c) CCl₅F₂OCFCCFCO(CF₅O)₅—CCl₅F₂OFCCFCF₅Cl —2%

The products are separated by fractional distillation. Characterization of the products: 19F-NMR

19F-NMR spectrum in p.p.m. with respect to CFCI₃ (p.p.m.=0) : 51.7, −55.3 (2F —OCF₂O —); −56.2 (3F C Cl₂OCF₂CCl₂O —); −57.8 (3F C Cl₂OCF₂CCl₂O —); −71.0 (2F —C F₃); −76.5 (1F —CFCI); −87.5 (3F C F₃OF —); −88.4, −90.7 (4F —OCFCCF₂O —).
traces the addition product to the olefin CF<sub>3</sub>O(CF<sub>3</sub>)<sub>2</sub>CFCF<sub>2</sub>OCFCICF<sub>2</sub>C1 (yield about 1% with respect to the converted acly fluoride).

This Example shows that the addition of olefins to hypofluorites having a structure similar to the product CF<sub>3</sub>O(CF<sub>3</sub>)<sub>2</sub>CFCF<sub>2</sub>OF occurs with extremely low yields.

### TABLE 1

<table>
<thead>
<tr>
<th>Ex.</th>
<th>—COF</th>
<th>T °C</th>
<th>Olefin addition</th>
<th>—COF</th>
<th>end groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3.64</td>
<td>5.5</td>
<td>1.51</td>
<td>10</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;F&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
<tr>
<td>2A</td>
<td>3.64</td>
<td>5.5</td>
<td>1.51</td>
<td>80</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;F&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
<tr>
<td>2B</td>
<td>3.64</td>
<td>5.5</td>
<td>1.51</td>
<td>10</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;F&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
<tr>
<td>2C</td>
<td>3.0</td>
<td>6.6</td>
<td>2.20</td>
<td>80</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;F&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
<tr>
<td>3</td>
<td>3.64</td>
<td>5.5</td>
<td>1.51</td>
<td>10</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;F&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
<tr>
<td>3A</td>
<td>1.85</td>
<td>4.7</td>
<td>2.54</td>
<td>80</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;F&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
<tr>
<td>3B</td>
<td>3.64</td>
<td>5.5</td>
<td>1.51</td>
<td>10</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;F&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
<tr>
<td>4</td>
<td>3.64</td>
<td>2.5</td>
<td>0.69</td>
<td>10</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;F&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
</tbody>
</table>

### TABLE 1A

Examples 4A-4C: reactions in a discontinuous way.

Conditions of diacyl fluoride fluorination (in the Table the mols of initial —COF end groups, of addition of the olefin to the hypofluorite, —COF conversion % and % by mols of the end groups CICF<sub>2</sub>FCFCIO — CF<sub>3</sub>CF<sub>2</sub>O — CF<sub>3</sub>O — formed in the reaction products; the % are calculated with respect to the amount of converted acly fluoride. The time of the fluorination reaction is 4 hours and the used catalyst is CF<sub>3</sub>(0.80 g).

<table>
<thead>
<tr>
<th>Ex.</th>
<th>—COF</th>
<th>F&lt;sub&gt;2&lt;/sub&gt;</th>
<th>F&lt;sub&gt;2&lt;/sub&gt;/—COF</th>
<th>C&lt;sub&gt;2&lt;/sub&gt;F&lt;sub&gt;4&lt;/sub&gt;</th>
<th>Olefin addition</th>
<th>—COF</th>
<th>C&lt;sub&gt;2&lt;/sub&gt;F&lt;sub&gt;4&lt;/sub&gt;</th>
<th>C&lt;sub&gt;2&lt;/sub&gt;F&lt;sub&gt;4&lt;/sub&gt;</th>
<th>C&lt;sub&gt;2&lt;/sub&gt;F&lt;sub&gt;4&lt;/sub&gt;</th>
<th>C&lt;sub&gt;2&lt;/sub&gt;F&lt;sub&gt;4&lt;/sub&gt;</th>
<th>C&lt;sub&gt;2&lt;/sub&gt;F&lt;sub&gt;4&lt;/sub&gt;</th>
<th>C&lt;sub&gt;2&lt;/sub&gt;F&lt;sub&gt;4&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>4A</td>
<td>3.64</td>
<td>2.0</td>
<td>0.55</td>
<td>10</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;F&lt;sub&gt;4&lt;/sub&gt;</td>
<td>CFCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>—COF</td>
<td>105</td>
<td>55</td>
<td>—</td>
<td>32</td>
<td>68</td>
</tr>
<tr>
<td>4B</td>
<td>3.64</td>
<td>2.0</td>
<td>0.55</td>
<td>10</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;F&lt;sub&gt;4&lt;/sub&gt;</td>
<td>CFCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>—COF</td>
<td>105</td>
<td>54</td>
<td>—</td>
<td>53</td>
<td>47</td>
</tr>
<tr>
<td>4C</td>
<td>3.64</td>
<td>1.92</td>
<td>0.53</td>
<td>20</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;F&lt;sub&gt;4&lt;/sub&gt;</td>
<td>CFCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>—COF</td>
<td>105</td>
<td>52</td>
<td>45</td>
<td>—</td>
<td>55</td>
</tr>
</tbody>
</table>

### TABLE 2

Examples 5 and 6: conditions of diacyl fluoride fluorination (abbrev. DACF in the Table), % conversion diacyl fluoride and % molar ratio of the end groups CICF<sub>2</sub>FCFCIO — CF<sub>3</sub>O — formed in the reaction products, calculated with respect to the mole of converted monohypofluorite (2). The fluorination reaction temperature is approximately 105 °C, the used olefin is CFCI<sub>2</sub> = CFCI and the reaction solvent C<sub>2</sub>F<sub>4</sub>.

<table>
<thead>
<tr>
<th>Ex.</th>
<th>—COF</th>
<th>F&lt;sub&gt;2&lt;/sub&gt;</th>
<th>F&lt;sub&gt;2&lt;/sub&gt;/—COF</th>
<th>time</th>
<th>Conv.</th>
<th>mono— COF</th>
<th>bis— COF</th>
<th>DacF</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>3.64</td>
<td>2.80</td>
<td>0.80</td>
<td>5</td>
<td>80</td>
<td>32</td>
<td>64</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>3.64</td>
<td>2.10</td>
<td>0.58</td>
<td>4</td>
<td>46</td>
<td>57</td>
<td>26</td>
<td>17</td>
</tr>
</tbody>
</table>

*abbreviation for end groups
TABLE 3

Examples 10, 10A-10E, 11-12: batch reactions

Conditions of dicarboxyfluoride fluorination (in the Table the moles of initial —COF end groups, of the olefin addition to the hypofluorite, —COF conversion, formula of the reaction products end groups, % by moles of said end groups and of CF₂O — in the reaction products; the % are calculated with respect to the amount of converted dicarboxyfluoride. The fluorination reaction has been carried out at -10° C. in 4 hours and the used catalyst is CaF₂ (0.90 g). In the column T° C. (1a) and (1b) the T° intervals are indicated in the respective Examples.

<table>
<thead>
<tr>
<th>Ex.</th>
<th>—COF</th>
<th>F₂</th>
<th>F₂ — —— COF</th>
<th>solv. olefin</th>
<th>T° C.</th>
<th>% moles</th>
<th>Formula</th>
<th>% moles</th>
<th>CF₂O—</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>3.64</td>
<td>5.5</td>
<td>1.51</td>
<td>CF₂F₄</td>
<td>CHCl — CHCl</td>
<td>-55</td>
<td>100</td>
<td>—OCH(CF₂Cl)</td>
<td>41</td>
</tr>
<tr>
<td>10A</td>
<td>3.64</td>
<td>5.5</td>
<td>1.51</td>
<td>CF₂F₄</td>
<td>CH₂ — CF₂</td>
<td>-80</td>
<td>100</td>
<td>—OCF(CF₂Cl)</td>
<td>39</td>
</tr>
<tr>
<td>10B</td>
<td>3.64</td>
<td>5.5</td>
<td>1.51</td>
<td>CF₂F₄</td>
<td>CH₂ — CF₂</td>
<td>-105</td>
<td>100</td>
<td>—OCH₂CF₂</td>
<td>24</td>
</tr>
<tr>
<td>10C</td>
<td>3.64</td>
<td>5.5</td>
<td>1.51</td>
<td>CF₂Cl₃</td>
<td>CHCl — CHCl₂</td>
<td>-80</td>
<td>100</td>
<td>—OCH₂F</td>
<td>3</td>
</tr>
<tr>
<td>10D</td>
<td>3.64</td>
<td>5.5</td>
<td>1.51</td>
<td>CF₂Cl₃</td>
<td>CH₂ — CH₂OCH₂</td>
<td>32</td>
<td>100</td>
<td>—OCH₂CF₂Cl</td>
<td>36</td>
</tr>
<tr>
<td>10E</td>
<td>3.64</td>
<td>2.10</td>
<td>0.58</td>
<td>CF₂Cl₃</td>
<td>maleic anhyd.</td>
<td>(1b)</td>
<td>100</td>
<td>—OCH₂ — —CHF</td>
<td>30</td>
</tr>
<tr>
<td>11</td>
<td>3.64</td>
<td>2.10</td>
<td>0.58</td>
<td>CF₂Cl₂</td>
<td>CH₂ — CHCl</td>
<td>-80</td>
<td>57</td>
<td>—OCH₂CFCl</td>
<td>51</td>
</tr>
<tr>
<td>12</td>
<td>3.64</td>
<td>1.82</td>
<td>0.80</td>
<td>CF₂F₆</td>
<td>CF₂OCCF₂ — CF₂</td>
<td>-105</td>
<td>49</td>
<td>—OCF(CF₂Cl)</td>
<td>90</td>
</tr>
</tbody>
</table>

The invention claimed is:

I. (Per)haloethers having formula (I)

X₁-R₂O—CF₂F₂CF₂O—CF₂X₂—CF₂X₃—CF₂X₄ (I),

wherein

X₁, X₂, X₃, X₄ have the following meanings:

1) X₁ and X₂ are, independently each from the other, F, H or Cl and X₃ and X₄ are independently each from the other, F, H, Cl or Br, wherein at least one of X₂ or X₄ is H or Cl, and at least one of X₁ or X₃ is H, Cl, or Br;

2) one of X₁ or X₂, and/or one of X₃ or X₄, is/are chosen from the following groups: —COOR₁ wherein R₁ is CₚHₗₙ, alkyl; —OC(O)CH₂ — CN; —NCO; —NCS; aryl, substituted with —NO₂ or non substituted; —NH —C(O)—NH₂; —CO(O)CH₃ — CH₂ — PO(O)(CH₂)₂; —PO(O)₂(H₂)₁₋₄; —SO₂F; wherein the remaining substituents of the group of X₁, X₂, X₃, and X₄ have the following meanings:

X₁ ≡ F, X₂ ≡ Cl, X₃ ≡ F, and X₄ ≡ Cl;

X₁ ≡ F, X₂ ≡ Cl, X₃ ≡ F, and X₄ ≡ H;

X₁ ≡ X₂ ≡ H, and X₃ ≡ X₄ ≡ Cl; or

X₁ ≡ X₂ ≡ X₃ ≡ Cl, and X₄ ≡ H;

3) one of X₁ or X₂, and/or one of X₃ or X₄, is/are chosen from the following groups:

a) C₁₋C₂₀ linear or branched per(halo)fluorinated alkyl;

b) C₁₋C₂₀ linear or branched per(halo)fluorinated oxyalkyl; wherein when the alkyl is per(halo), there are one or more atoms of Cl and/or Br;

c) C₁₋C₂₀ linear or branched alkyl, optionally containing one or more functional groups, chosen between COOR₁ wherein R₁ is C₁₋C₄ alkyl; —OC(O)CH₂; —CN; —NCO; —NCS; aryl, substituted with —NO₂ or non substituted; —NH —C(O)—NH₂; —OC(O)CH₃ — CH₂ — PO(O)(CH₂)₂; —PO(O)₂(H₂)₁₋₄; —SO₂F; and/or hydrated organic anhydrides chosen from the group of linear anhydrides of organic C₁₋C₄ mono-carboxylic acids or cyclic anhydrides of C₄₋C₆ dicarboxylic acids; wherein the remaining substituents of the group of X₁, X₂, X₃, X₄, independently each from the other, are F, H, Cl or Br;

4) one of X₁ or X₂, together with one of X₃ or X₄, and the two carbon atoms of the group —CX₂—CFX₃—CFX₄ form cyclic fluorinated or hydrogenated anhydrides or imide compounds, containing 4-6 carbon atoms in the ring, wherein the remaining substituents between X₁ or X₂ and between X₃ or X₄, independently each from the other, are F, H, Cl or Br;

4a) X₁ and X₄, together with the relevant carbon atom to which they are attached, form a cyclic anhydride ring having 4 carbon atoms; X₁ and X₄ independently each from the other, are F, H, Cl or Br;

X has the following meanings:

F, linear or branched C₁₋C₃ per(halo)alkyl; —[O]₁CF₂CF₂OCX₂ — CF₂X₁ — [O]₁CF₂C(O)F; wherein

T° = 0 when L = 1 and Rᵣ = Rᵣᵣ as defined below;

T° = 1 when L = 1 and Rᵣ = Rᵣᵣ as defined below;

when L = 1 and Rᵣ = Rᵣᵣ defined below, X is also C₁₋C₄ perfluoroalkyl;

L < 1, when L < 0, X must not have the following meanings:

F; —[O]₁CF₂CF₂OCX₂ — CF₂X₁ being T° = 0, X₁ = F, X₂ = Cl, X₃ = F, X₄ = Cl;

C₁₋C₃ perfluoroalkyl when X₀ = F and X₁ = Cl, X₂ = F; when L = 1, Rᵣ = Rᵣᵣ or Rᵣᵣᵣ, wherein

Rᵣᵣᵣ = C₁₋C₂₀ perfluoroalkylene; Rᵣᵣᵣᵣ = perfluoroalkylen having formula:

—[O]₁CF₂(OFCF₃)ₘ(OFCF₂Cl)ₘ(OFCF₃Cl)ₙ(OFCF₃F)ₙ

wherein m, n, p, q, r are integers such that:

m is 0 to 100;

n is 0 to 100;
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p is 0 to 60;
p is 0 to 60;
q is 0 to 60; m+n+p+r+q=1; and
the average molecular weight of R1 from 66 to 12,000.

2. (Per)haloethers according to claim 1, wherein when
R1=R1' the perfluoroalkylene has the following formula:

$$\text{OCF}_2\text{CF}_2\text{O} - \text{CF}_2\text{CF}_2\text{O} - \ldots - \text{CHCl}_2\text{CFCl}_2$$

wherein m and n independently one from the other have
the above values; when both m and n are present, nn ranges
from 0.1 to 6.

3. (Per)haloethers having the following formulas:

$$\text{CF}_2\text{CF}_2\text{O} - \text{CF}_2\text{CF}_2\text{O} - \ldots - \text{CHCl}_2\text{CFCl}_2$$

wherein m/n = 4.3 and the molecular weight of the perfluoro-
alkylene chain - (CF2CF2O)n(CF2O)m is 620.

4. (Per)haloethers according to claim 1, wherein X1, X2,
X3, X4 are selected from the group consisting of: F, H, and Cl.

5. (Per)haloethers according to claim 1, wherein X1=F,
X2=Cl, X3=Cl, X4=F, X5=Cl.

6. (Per)haloethers according to claim 1, wherein X1=F,
X2=H, X3=F, and X4=Cl.

7. (Per)haloethers according to claim 1, wherein X1=H
and X2-X4=Cl.

8. (Per)haloethers according to claim 1, wherein
X1=X2=Cl and X3=H.

9. (Per)haloethers according to claim 1, wherein one of X1,
or X2, or X1 or X2 is/is chosen from the following
groups: - COOR, wherein R' is C1-C3 alkyl; - CN;
- NC=O; - NCS; ary1, substituted with -NO2 or non
substituted; and - SO2F.

10. (Per)haloethers according to claim 1, wherein 3a) is
Cl-C5, linear or branched per(halo)fluorinated alkyl.

11. (Per)haloethers according to claim 1, wherein 3a) is
linear or branched (per)fluoralkyl.

12. (Per)haloethers according to claim 1, wherein 3b) is
C1-C5, linear or branched or heated (per)fluorinated oxalkyl,
wherin when the alkyl is per(halo), there are one or more
atoms of Cl or Br.

13. (Per)haloethers according to claim 1, wherein 3b) is
linear or branched (per)fluoroalkyl.

14. (Per)haloethers according to claim 1, wherein 3a) and
3b) each contain one or more functional groups chosen from:
- COOR, wherein R' is C1-C3 alkyl; - OC(O)CH3;
- CN; - NC=O; - NCS; aryl, substituted with -NO2 or non
substituted; - NH-C(O)-NH; - OC(O)CH3; - PO(2)
(C1H3)2; - PO(2)(C1H3)2; or - SO2F; and/or from fluori-
inated or hydrogenated organic anhydrides chosen from
the
group of linear anhydrides of organic C₁-C₄ mono-carboxylic acids or cyclic anhydrides of C₄-C₆ dicarboxylic acids.

15. (Per)haloethers according to claim 1, wherein 3a) and
3b) each contain one or more functional groups chosen from:
—COOR¹, wherein R¹ is C₁-C₃ alkyl; —OC(O)CH₃;
—CN; —NCO; —NCS; aryl, substituted with —NO₂ or non
substituted; —NH—C(O)—NH₂; —OC(O)₂CH₃; —P(O)
(C₃H₇)₂, —P(O)₂(C₃H₇), or —SO₂F and/or from fluori-
nated or hydrogenated cyclic anhydrides of C₄-C₆ dicarboxy-
lric acids.

16. (Per)haloethers according to claim 1, wherein 3c) is
C₁-C₃ alkyl or branched alkyl, optionally containing one or
more functional groups, chosen from: COOR¹, wherein R¹
is C₁-C₃ alkyl; —OC(O)CH₃; —CN; —NCO; —NCS; aryl,
substituted with —NO₂ or non substituted; —NH—C(O)—
NH₂; —OC(O)₂CH₃; —P(O)(O)(C₃H₇), —P(O)₂(C₃H₇), —SO₂F and hydrogenated organic anhydrides chosen from
the group of linear anhydrides of organic C₁-C₄ mono-car-
boxylic acids or cyclic anhydrides of C₄-C₆ dicarboxylic
acids; wherein the remaining substituents of the group of X₁,
X₂, X₃, X₄, independently each from the other, are F, H, Cl or
Br.

17. (Per)haloethers according to claim 1, wherein one of
X₁, or X₂, together with one of X₃, or X₄ and the two carbon
atoms of the group —CX₅X₆CFX₇X₈ form cyclic fluorinated
or hydrogenated anhydride or imide compounds, containing
4 carbon atoms in the ring, wherein the remaining substitu-
ents between X₁, or X₂, and between X₃, or X₄, have the
meanings as defined under 1).

18. (Per)haloethers according to claim 1, wherein X is
linear or branched C₁-C₃ (per)fluoroalkyl, wherein optionally
one fluorine atom is substituted with one chlorine atom.

19. (Per)haloethers according to claim 1, wherein when
L=1, RF=RF or RF', the average molecular weight of RF'
is 70 to 3,000.

20. (Per)haloethers of claim 2, wherein when m and n
independently one from the other have a value of 0 to 20.

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